



Citation for published version:

Price, GJ, Lenz, EJ & Ansell, CWG 2002, 'The effect of high-intensity ultrasound on the ring-opening polymerisation of cyclic lactones', *European Polymer Journal*, vol. 38, no. 9, pp. 1753-1760.
[https://doi.org/10.1016/S0014-3057\(02\)00056-3](https://doi.org/10.1016/S0014-3057(02)00056-3)

DOI:

[10.1016/S0014-3057\(02\)00056-3](https://doi.org/10.1016/S0014-3057(02)00056-3)

Publication date:

2002

Document Version

Peer reviewed version

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The Effect of High Intensity Ultrasound on the Ring Opening Polymerisation of Cyclic Lactones

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Abstract

High intensity ultrasound has been applied to the ring-opening polymerisation of δ -valerolactone and ϵ -caprolactone catalysed by dibutyl tin dilaurate. Sonication was found to accelerate the polymerisation. In the case of δ -valerolactone, sonication also promoted a depolymerisation reaction so that the molecular weight fell during later stages of the reaction. Copolymers of the two monomers were synthesised and the use of ultrasound led to preferential incorporation of ϵ -caprolactone into the material, probably due to degradation of the valerolactone sequences.

Keywords: polylactones; sonochemistry; cavitation; polymerisation rates; ultrasound.

Introduction

There has recently been considerable interest in the synthesis of aliphatic polyesters. A commonly employed synthetic method is the ring-opening polymerisation^{1,2} of the appropriate cyclic lactone such as ϵ -caprolactone, CL, or δ -valerolactone, VL. These polymers have been used for a number of applications but the major interest is that they are biodegradable to relatively harmless products and hence have been investigated as biomaterials³⁻⁵ including drug delivery carriers and matrices to support cell growth in tissue engineering.

The ring opening reaction can be initiated by anionic or cationic species and is often performed in solution where high molecular weight polymers can be obtained, particularly for CL. However, for many processes, the polymerisation of bulk lactone is preferred although generally only lower molecular weight species arise. In these reactions, the monomer conversion and the ultimate chain length are limited by the ring-chain equilibrium that is set up. For CL, the equilibrium lies heavily in favour of the polymer although for VL, substantial amounts of monomer remain at equilibrium. The homopolyesters produced from CL and VL are semi-crystalline, low melting solids. It was of interest to determine whether operating the polymerisation under ultrasound could influence the yields, the achievable molecular weights and/or the degree of crystallinity in homo- and co-polymers.

The use of high intensity ultrasound has become a useful tool in synthetic chemistry^{6,7} including a number of polymerisation reactions^{8,9}. Most sonochemical effects can be attributed to cavitation¹⁰, the growth and explosive collapse of microscopic bubbles as the sound wave propagates through the fluid. This can result in extreme conditions of temperature (> 2000K) and pressure (>500 bar) on a microsecond timescale¹¹. The motion of fluid around the bubbles is rapid resulting in very efficient mixing or the formation of jets of liquid against solid surfaces⁸. The rapid motion can result in effective shear degradation of polymer chains over a certain size in the vicinity of cavitation bubbles¹².

The most studied system in polymer synthesis is radical polymerisation in vinyl monomers. Ultrasound can obviate the need for thermal initiators and hence can be applied at lower temperatures than are required for conventional initiators. Control over the molecular weight and polydispersity can also be achieved^{13,14}.

There have been relatively few instances of ultrasound being applied to step-growth polymerisations. Watanabe *et al.* used an ultrasonic cleaning bath to prepare aromatic polyformals¹⁵ while Long¹⁶ patented reactors incorporating ultrasonically vibrating walls which could be used for spatial and rate control of several polyurethane systems and were useful for producing foams. Application to ring-opening systems is illustrated by the work of Stoessel¹⁷ who reported the use of very high intensity ultrasound to promote the polymerisation of small cyclic polycarbonate oligomers. Other work in this area has involved the polymerization of cyclic siloxanes¹⁸.

A major impetus for this study comes from work of Ragaini¹⁹ *et al.* who showed that ultrasound enhanced the ring opening of ϵ -caprolactam to form nylon-6, allowing a single step polymerization. High molecular weight materials with narrower distributions were formed in shorter reaction times than when using the conventional process and sonication allowed the polymerization to be run at lower temperatures than under conventional conditions.

This communication presents an initial study of the effects of ultrasound on the polymerisation and copolymerisation of CL and VL using dibutyltin dilaurate as the catalyst and 1,6-hexane diol as the hydrogen donor which acts as a promoter or initiator²⁰.

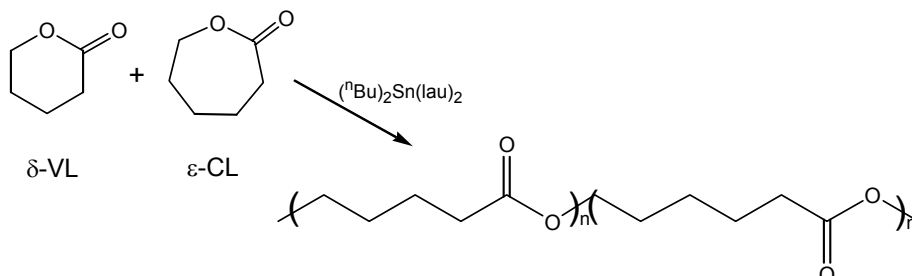
Experimental

Polymerisation methods: The source of ultrasound used was a Sonics and Materials VC50 horn system. This apparatus couples the ultrasound directly into the reaction medium through a titanium horn. The configuration used, illustrated in Figure 1, has been described previously¹⁴. The reaction temperatures were controlled to ± 2 °C. Around ambient temperature, this was achieved by circulating water through a glass jacket around the reaction container. At higher temperatures a non-jacketted reaction vessel was placed in a heated silicone oil bath. Reactions conducted without ultrasound were performed with vigorous mechanical stirring. Sonication intensities were measured calorimetrically²¹.

Figure 1 near here

In a typical polymerisation, 15 - 20 g of the cyclic lactone was added to the flask along with hexane diol (1:30 molar ratio diol:lactone – see below) and approximately 0.10 g dibutyltin dilaurate. After removal of oxygen with nitrogen gas bubbling, the reaction was heated to the

appropriate temperature and samples (~ 0.25 g) were periodically removed and quenched in liquid nitrogen to stop the reaction. The polymers were purified by reprecipitation into hexane from dichloromethane before being dried *in vacuo* at $80\text{ }^{\circ}\text{C}$.



Materials: Two lactones were used in the study; δ -valerolactone (99 %) was obtained from Lancaster chemicals and ϵ -caprolactone (99+ %) from Aldrich. All solvents and other reagents used were of Reagent grade or better and were obtained from Aldrich Ltd.

Analytical methods: Infra-red spectra were recorded as films on NaCl plates using a Perkin-Elmer PE983 spectrometer. NMR spectra were recorded on solutions in CDCl_3 on a JEOL GX400 spectrometer using TMS as an internal standard. Differential Scanning Calorimetry was conducted on a Dupont 910 calorimeter using a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ with indium and water used as calibration standards. Molecular weights were estimated using a Bruker LC21/41 Gel Permeation Chromatograph with tetrahydrofuran as the eluent at a flow rate of $1\text{ cm}^3\text{ min}^{-1}$. Calibration of the 60 cm, $5\text{ }\mu\text{m}$ 'mixed' pore size 'PLGel' column was performed using polystyrene standards (Polymer Laboratories Ltd) with molecular weights ranging from 9200 to $1.03 \times 10^6\text{ g mol}^{-1}$. A number of synthesised lactone polymers were analysed by GPC viscometry in an effort to determine the parameters needed for a 'universal calibration'. However, the polymers produced were of relatively low molecular weight and this technique is not well suited to this range. As a result, the values derived were not consistent and not in good agreement with previously reported values²² which themselves vary quite widely. The values reported below are "polystyrene equivalents". The viscometry results suggest that the true values are somewhat smaller than those reported.

Results and Discussion

Initial work concentrated on conventional thermal polymerisations to give a basis for comparison with the sonochemical results. It is known that the polymer molecular weight depends critically on the ratio of lactone to initiator used²⁰. Figure 2 shows the resulting molecular weights when δ -valerolactone was polymerised using 1% dibutyltin dilaurate catalyst with varying amounts of 1,6-hexane diol at 160 °C for 6 hr. For subsequent work, a ratio of 30:1 was chosen as a compromise between accuracy in preparing reactants and reasonable molecular weights. Conversely, the final polymer molecular weight was found, as illustrated in Figure 3, to be relatively insensitive to the reaction temperature. As expected, the reaction occurs faster at higher temperatures but the final molecular weight does not vary significantly within the range investigated.

Figures 2 & 3 near here

Having established suitable reaction conditions, polymerisations of VL were conducted under varying intensities of ultrasound. Figure 4 shows molecular weight results for polymerisations at an intensity of 25.4 W cm^{-2} at 150 °C and 170 °C. It should be noted that as the polymer is produced, the increased viscosity makes cavitation more difficult to sustain. Thus, the results presented here are at relatively low conversions ($\sim 20 - 40 \%$). The reactions were stopped at this point in order to maintain temperature control. Sonication of a viscous gel leads to considerable temperature increases. In each case, the sonochemical reaction produced a larger amount of polymer for the same reaction time. Figure 4 shows that, initially, the expected rise in molecular weight mirrors that in the thermal reaction although the chain growth occurs more rapidly under sonication. In contrast to the “silent” polymerisations (i.e. those conducted under “thermal” conditions in the absence of ultrasound), the average molecular weight reaches a pronounced maximum and then falls steadily during prolonged sonochemical reaction. At the higher temperature, the maximum value was reached earlier in the reaction.

Figure 4 near here

Similar behaviour was observed for experiments at four different ultrasound intensities as shown in Figure 5 although the effect is more pronounced at higher intensities. Also shown are the values from a conventional polymerisation. The corresponding polydispersities for the polymers produced at 170 °C are shown in Figure 6, the pattern being similar to that of the

molecular weights. As the intensity of the ultrasound was increased, the molecular weight and polydispersity maximum occurred earlier in the reaction. There was no evidence of the molecular weight lowering degradation process in the thermal polymerisations on the timescale of the reactions reported here.

Figures 5 & 6 near here

A number of factors associated with sonication of systems could account for these results. Firstly, sonication is often accompanied by significant temperature rises. However, in the experiments described here, care was taken to monitor and control the bulk temperature, usually to within ± 2 °C, a variation that is too small to adequately account for the effects observed. Sonication can promote very efficient mass transfer and mixing. In other polymerisations^{18, 23}, it has been demonstrated that this can lead to good distribution of catalysts through reactants leading to efficient initiation of polymerisation, although it should be noted that these were not homogeneous reactions. Gorda²⁴ showed that the tin catalyst was necessary for efficient propagation during the reaction whereas the “initiation” – reaction of the lactone with an amine – took place in the absence of catalyst. Better distribution of the catalyst through the reaction would therefore explain the enhanced rate of chain growth seen in the sonochemical reactions. However, in these systems the catalyst is soluble and, with the experimental procedures used, should be well dispersed prior to the reaction commencing. The harsh conditions of temperature and shear generated around collapsing cavitation bubbles could lead to breakdown of the monomer. This has been invoked in other ring-opening reactions¹⁷ but this would seem to be more likely to generate radical species and this polymerisation is not very sensitive to radical species. Ragaini¹⁹ showed that caprolactam could be melt polymerised without the addition of the usual initiator, water, suggesting that reactive intermediates could be generated by sonication alone. Thus, the faster reaction is probably due to a combination of sonochemically generated intermediates combined with extremely efficient mixing and mass transfer. This will be further discussed below.

Another possible explanation of the results would involve the well known shear degradation²⁵ associated with cavitation collapse to explain the molecular weight profile during the polymerisation. However, work on a wide range of polymer – solvent combinations suggests that this only becomes significant when the molecular weight exceeds ~ 20000 – 25000

depending on the intensity used. Taking into account the observed molecular weights and polydispersities in this work (while noting that they are polystyrene equivalent values) it is unlikely that the polymers produced included significant amounts of material of this chain length.

It is known that thermolysis of the backbone ester groups can occur during prolonged heating. Saotome²⁶ reported that poly(VL) showed substantial weight loss on heating to 200 °C due to a depolymerisation reaction. This usually occurs via cleavage of the acyl-oxygen bond after a hydrogen abstraction²⁷ although decarboxylation can also occur. If the sonochemical enhancement of the reaction is due to efficient dispersal and/or activation of the catalysts, this may also promote the degradation. It is likely that a sonochemical acceleration of similar processes is responsible for the effects described here, with the polymerisation and degradation processes occurring concurrently and equilibrium being approached faster under ultrasound. Further evidence for the lack of shear effects can be gained by considering the rate of the degradation. Figure 7 shows the degradation phase of the reaction plotted as a first order process. Good agreement is seen lending support to a thermally stimulated cleavage of the chains. Careful analysis of ultrasonic shear degradation results has shown²⁵ that it is not a first order process whereas thermal degradations often obey this kinetic law²⁷.

Figure 7 near here

For comparison, reactions were conducted using CL as the monomer. The conditions were identical with those used above and the results are shown in Figure 8. The ultrasonically promoted reaction proceeded somewhat faster than the “silent” reaction under the same conditions. However, the differences were small. After approx. 150 min, the sonicated system became too viscous to support cavitation so that the reactions were terminated. It would appear that, at this point in the reaction, the maximum molecular weight achieved was again similar under the two sets of conditions. However, in contrast to the poly(valerolactones), no lowering of molecular weight due to degradation was observed in the ultrasound reactions. It is known that poly(CL) is more stable to thermal degradation than poly(VL) and the equilibrium concentration of monomer is very small in CL polymerisations.

Figure 8 near here

In order to assist with understanding the mechanism of action of the ultrasound, a series of experiments was performed in which the initiator and/or catalyst was omitted. Figure 9 shows

the evolution of molecular weight in the reaction of δ -valerolactone at 150 °C with the tin catalyst but no diol. It should be noted that the purely thermal reaction at the same temperature yielded very small amounts (2 - 3 %) of polymer. It is clear that in the presence of ultrasound, a degree of polymerisation can take place without the need for the initiator. Higher molecular weight polymers were obtained than when the diol was added, as expected since there will presumably be a lower number of growing chains in the system. It is noticeable that the degradation process does not occur in the reactions where no diol is added. The pattern in the results is also less discernable in these systems. The larger variation in the results may indicate that mixing the catalysts is less effective in the absence of ultrasound.

Figure 9 near here

Omitting the tin catalysts from the polymerisation had a greater effect on the reaction. For the silent reaction, a very low (< 1%) yield of polymer was obtained with a molecular weight of approximately 4000 which did not change on extended reaction. When ultrasound was used, a larger yield was obtained but the molecular weights were the same as in the silent case. It is clear that some reaction is taking place but the results seem to confirm that the catalyst is necessary for effective propagation.

Finally, samples of the monomer were subjected to heating or sonication with no added initiator or catalyst. As expected, there was no reaction in the solely heated case. However, significantly, some polymer was recovered from the sonicated reactions with molecular weights similar to those produced when the catalyst was omitted from the reaction. It is known that water can act as an initiator¹ and, since the lactones were not extensively dried in this work, this may be partly responsible. However, since no reaction took place in the absence of ultrasound, it would appear that some intermediate generated during cavitation can initiate the ring-opening.

As noted above, the enhanced mixing and mass transport will accelerate the reaction although the effect is likely to be less important in this homogeneous system than in previously studied heterogeneous reactions. The mechanism of the tin catalysis of the reaction has been investigated by several workers. Kricheldorf²⁸ and Duda and et al.²⁹ showed that the reaction proceeds at the less stable Sn — OR bond at the catalyst. Propagation occurs via an acyl — oxygen bond scission in the lactone following a coordination-insertion reaction at the catalyst site. Kricheldorf has suggested that a number of active tin species are formed during the reactions.

One mode of operation by which the sonochemical enhancement could occur is by promotion of these active species. A number of unusual ligand insertion reactions generating unusual coordination species have been reported³⁰ to occur under sonication and it may be that sonochemical decomposition of either the catalyst (less likely) or the monomer or diol leads to attack onto the tin and activation of a tin — alkoxide bond. Further studies of the polymer structure including the nature of the end-groups will be necessary to determine this mechanistic detail. Further support for this suggestion of the modification of the catalyst behaviour comes from the production of polymer in the absence of added diol in contrast to the thermal reactions. The formation of polymer under these circumstances suggests that a species generated by sonochemical methods can initiate the reaction even though the tin catalyst is necessary for efficient propagation.

One of the results of cavitation is the generation of high temperatures in the collapsing bubble. These temperatures are sufficiently high to pyrolyse any volatile material that enters the bubble and so, while they may be responsible for the generation of active intermediates, they play no part in accelerating the chemical reactions responsible for polymerisation. Some of this heat will be conducted into the interfacial region around the bubbles and may result in some thermal effects. However, significant enhancement of reactions due to this effect has not been reported. Indeed, sonication has been applied⁶ to thermally relatively labile compounds so that it is unlikely to affect the reaction to a significant degree. It is also likely that such an effect would lead to reactions over a wide range of temperatures and hence a variation in product or polydispersity during polymerisations might be expected. This has not been observed.

In the final part of this initial study, reactions were performed using mixtures of the two lactone monomers. Copolymerisations were carried out at 150 °C using a 30:1 molar ratio of lactone to hexane diol with dibutyltin dilaurate as above. As with homopolymerisation, ultrasound was effective at promoting the formation of copolymers at faster rates than by conventional thermal polymerisation as shown in Figure 10. The results again show that the reactions are accelerated under ultrasound and that higher molecular weight polymers are formed than in the equivalent silent reaction. As expected from the homopolymerisation results, polymers with higher amounts of caprolactone had higher molecular weights. It was also noticeable that the

degradation reaction which results in lowering of chain length was only seen where the composition contained relatively large amounts of VL.

Figure 10 near here

Table 1 shows the polymer composition as determined by ^1H nmr spectroscopy in the usual manner³¹ compared with the initial ratio of the monomers in the reaction mixture. This confirms that caprolactone was preferentially included in the copolymers over that in the feed mixture. The data also show that this preference is enhanced under ultrasound. It has been speculated³² that the preferential incorporation might be due to the relative rates of ring opening of the two monomers. Storey and co-workers³¹ measured the reactivity ratios for this copolymerisation catalysed by tin octanoate and found that a CL terminated chain added VL four times faster than CL while a VL terminated chain reacted twice as fast with CL. Thus, enhanced incorporation of VL might be expected at low conversions. Their explanation of the enhanced incorporation of CL was that, particularly at high conversion, the depolymerisation of valerolactone became important leading to longer sequences of CL. The latter explanation would seem more likely in the work reported here given the observations in the VL homopolymer system where the ultrasound was seen to accelerate the degradation of poly(VL).

The melting points of the materials were measured by DSC and are also shown in Table 1. The melting points of the homopolymers are in good agreement with Literature values³¹ and the use of ultrasound in their synthesis had no significant effect. The values for the copolymers were depressed in comparison with the homopolymers indicating that the materials were not homopolymer blends but were true copolymers. In these materials, the T_m values were dependent on whether ultrasound was used, the trend suggesting that the sonochemically produced materials contained a greater proportion of caprolactone.

Figure 11 shows the melting point of all the materials produced as a function of their true composition as given by NMR. All the values lie on the same smooth curve indicating that the differences between samples are simply due to compositional differences rather than any fundamental effect of the ultrasound.

Figure 11 near here

Conclusions

It has been shown that high intensity ultrasound can be used to accelerate the ring opening polymerisations of cyclic lactones. This was due to efficient mixing of the system and the formation of reactive intermediates at the tin catalyst which could initiate the reaction. Higher molecular weights were initially produced under ultrasound but, in the case of poly(valerolactone) the values fell due to a degradation. It appears that the sonochemical reaction proceeds toward equilibrium at a faster rate. It would be interesting to further study this reaction in solution where the increasing viscosity would not be a problem. Copolymerisations are also enhanced but the degradation of the VL sequences leads to enhancement of the amount of CL in the copolymers. The sonochemical production of the copolymer had no effect on its melting point compared with a conventionally produced material of the same composition.

Acknowledgements

The award of an EPSRC research studentship (to E.J.L.) and CASE funding from Smith and Nephew Ltd are gratefully acknowledged. We are also grateful to one of the referees for valuable suggestions regarding the work.

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Table 1. DSC melting temperatures and compositions of lactone copolymers

% caprolactone in feed	Melting Point / °C		% caprolactone in copolymer	
	<i>Thermal</i>	<i>Ultrasound</i>	<i>Thermal</i>	<i>Ultrasound</i>
0	52	53		
22.6	36	26	29 ± 2	46 ± 2
46.7	13	15	61 ± 2	68 ± 2
72.5	36	41	83 ± 2	91 ± 3
100	54	53		

Captions for Figures.

1. Schematic diagram of sonochemical polymerisation apparatus
2. Effect of hexane diol concentration on poly(valerolactone) molecular weight for reaction at 160 °C.
3. Poly(valerolactone) molecular weights for polymerisations at the indicated temperatures (°C)
4. Comparison of poly(valerolactone) molecular weights for thermal and sonochemical reactions at the indicated temperatures.
5. The effect of ultrasound intensity (indicated in W cm^{-2}) on the molecular weight of poly(valerolactone)s polymerised at 150 °C .
6. The effect of ultrasound intensity (indicated in W cm^{-2}) on the polydispersity of poly(valerolactone)s polymerised at 150 °C .
7. First order rate plot for the degradation of poly(valerolactone) during reactions at 150 °C. (I indicates the ultrasound intensity in W cm^{-2}).
8. Comparison of poly(caprolactone) molecular weights for thermal and sonochemical ($I = 18.4 \text{ W cm}^{-2}$) reactions at 150 °C.
9. The effect of omitting hexane diol from valerolactone polymerisations at 150 °C.
10. Comparison of molecular weights of poly(caprolactone-co-valerolactone) during thermal and sonochemical ($I = 18.4 \text{ W cm}^{-2}$) polymerisations at 150 °C. The initial molar percentage of CL in the reaction is as shown.
11. The variation of melting temperature with composition for poly(caprolactone-co-valerolactone) copolymers.

Reaction scheme

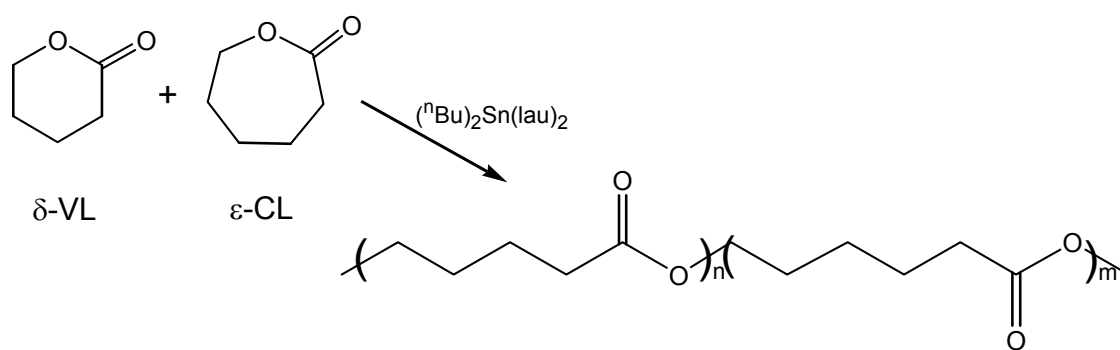


Figure 1

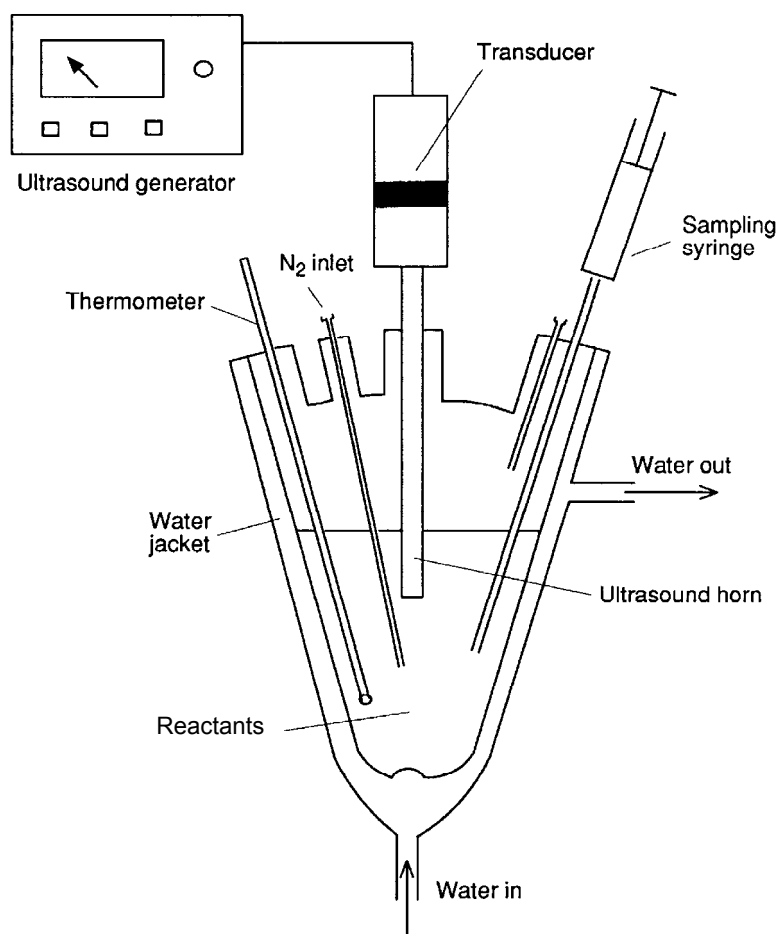


Figure 2

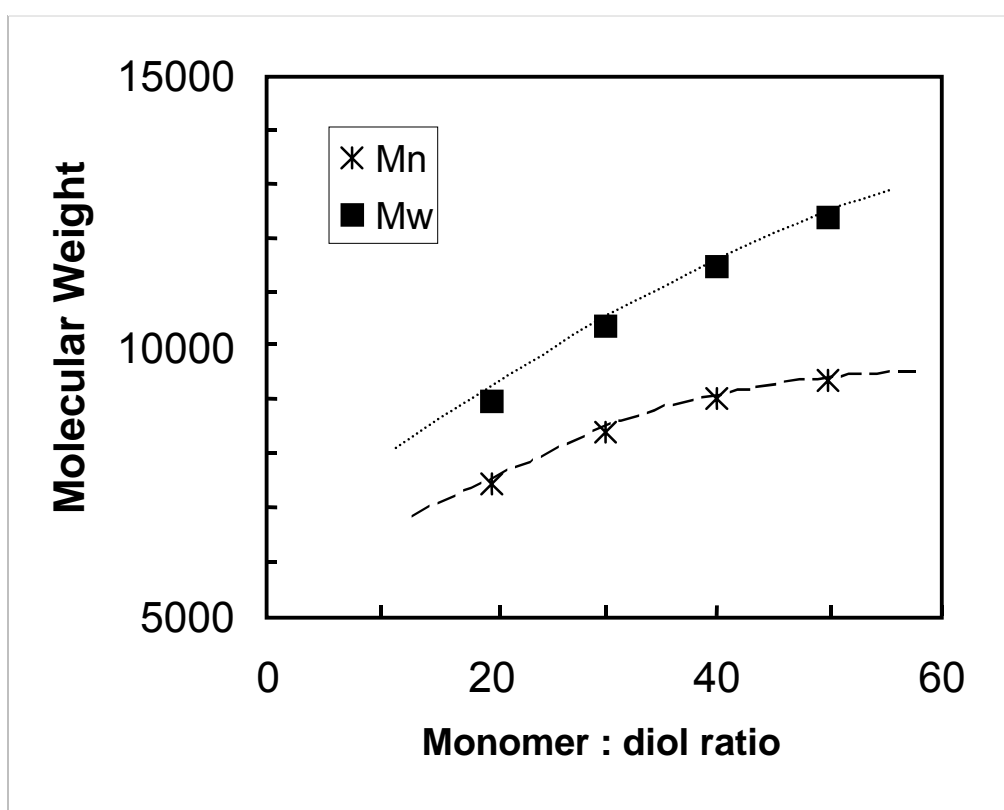


Figure 3

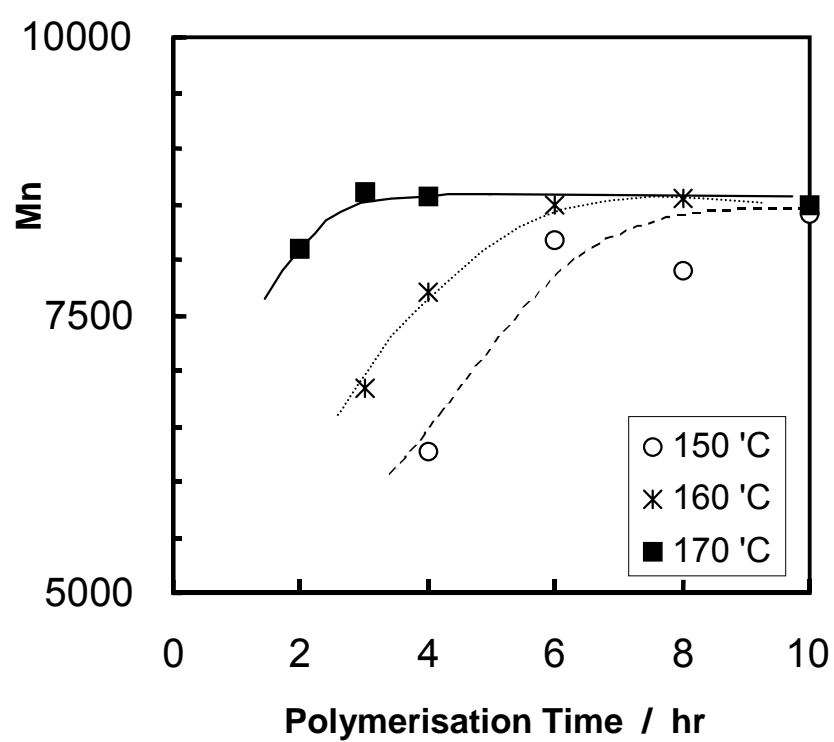


Figure 4

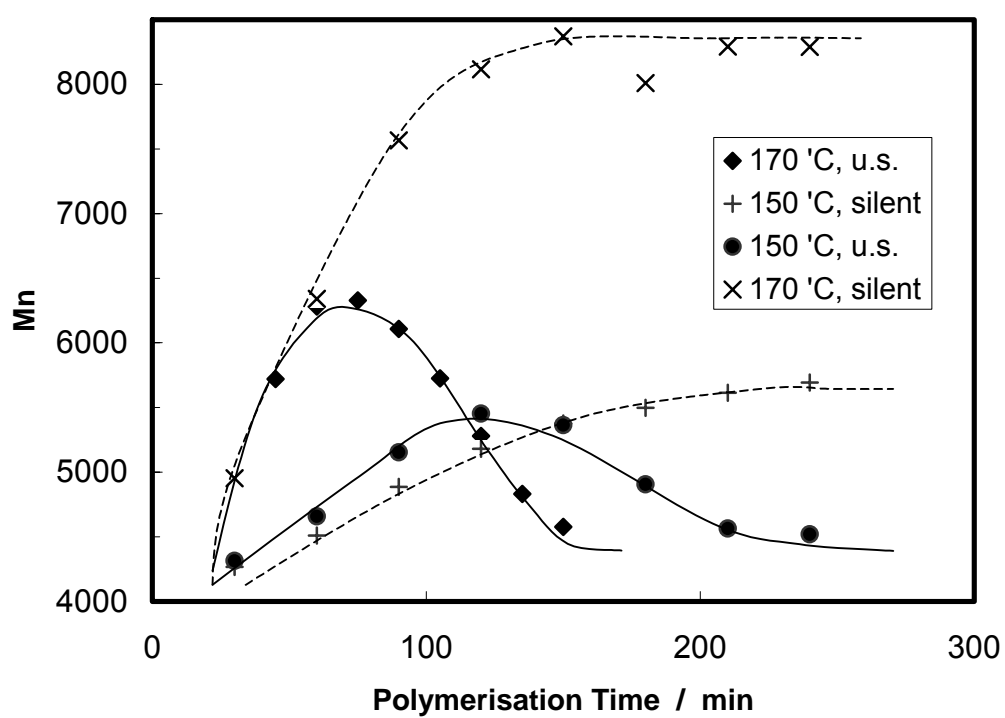


Figure 5

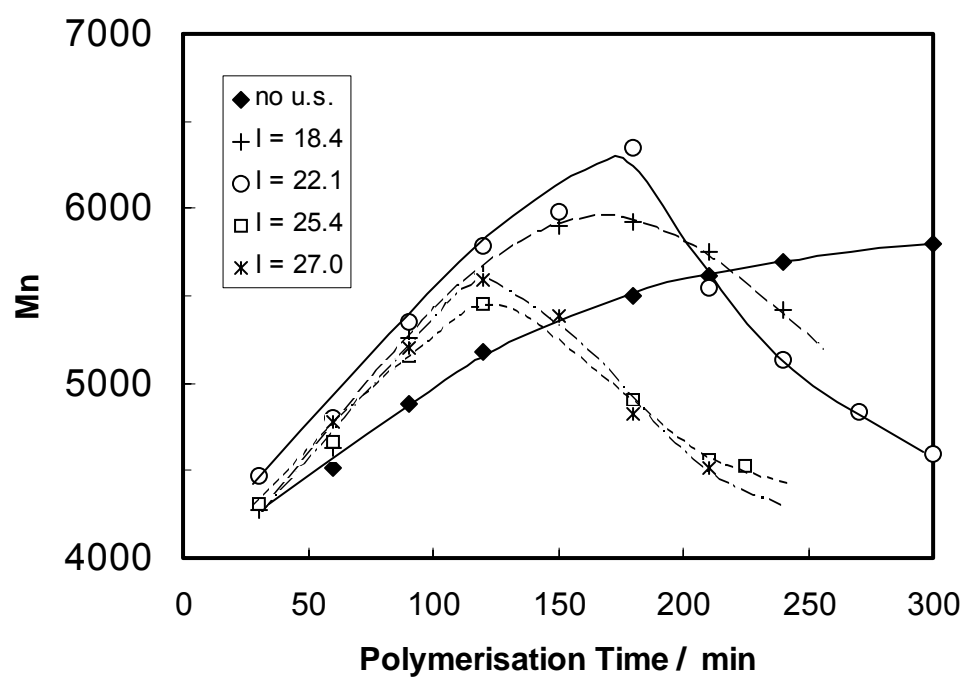


Figure 6

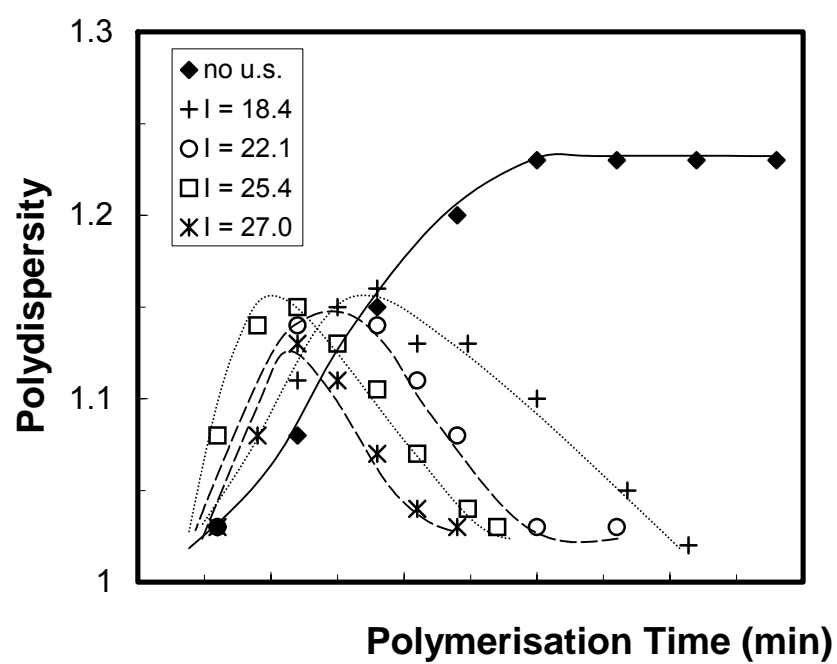


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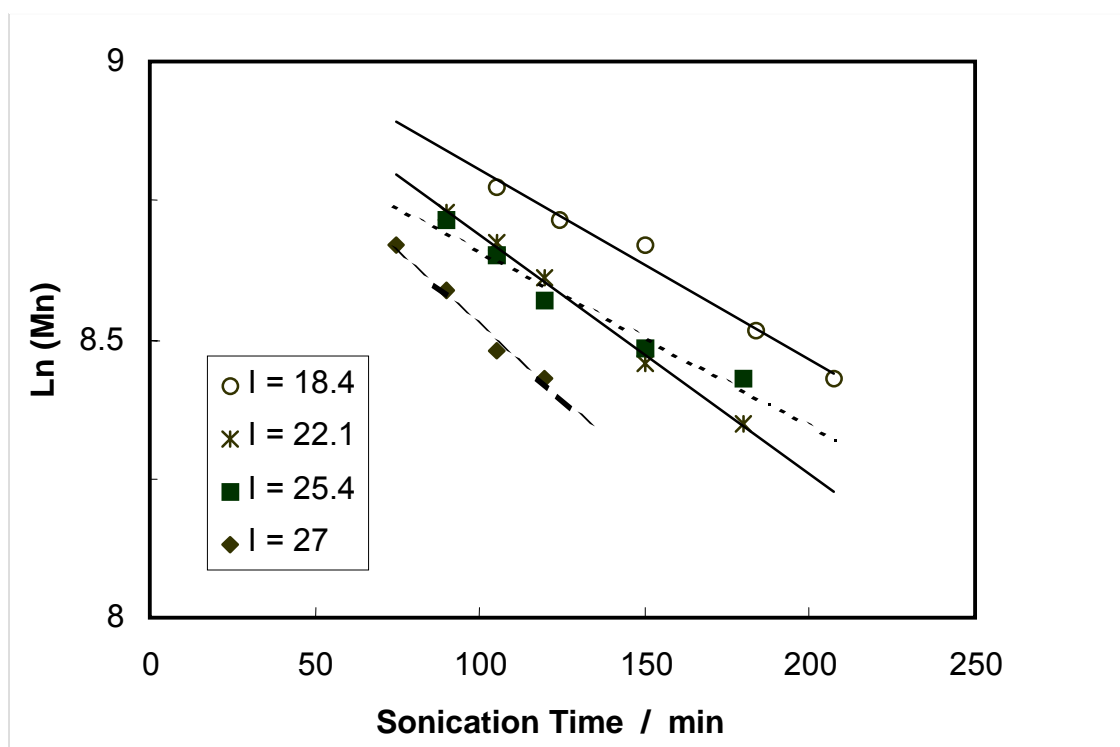


Figure 8

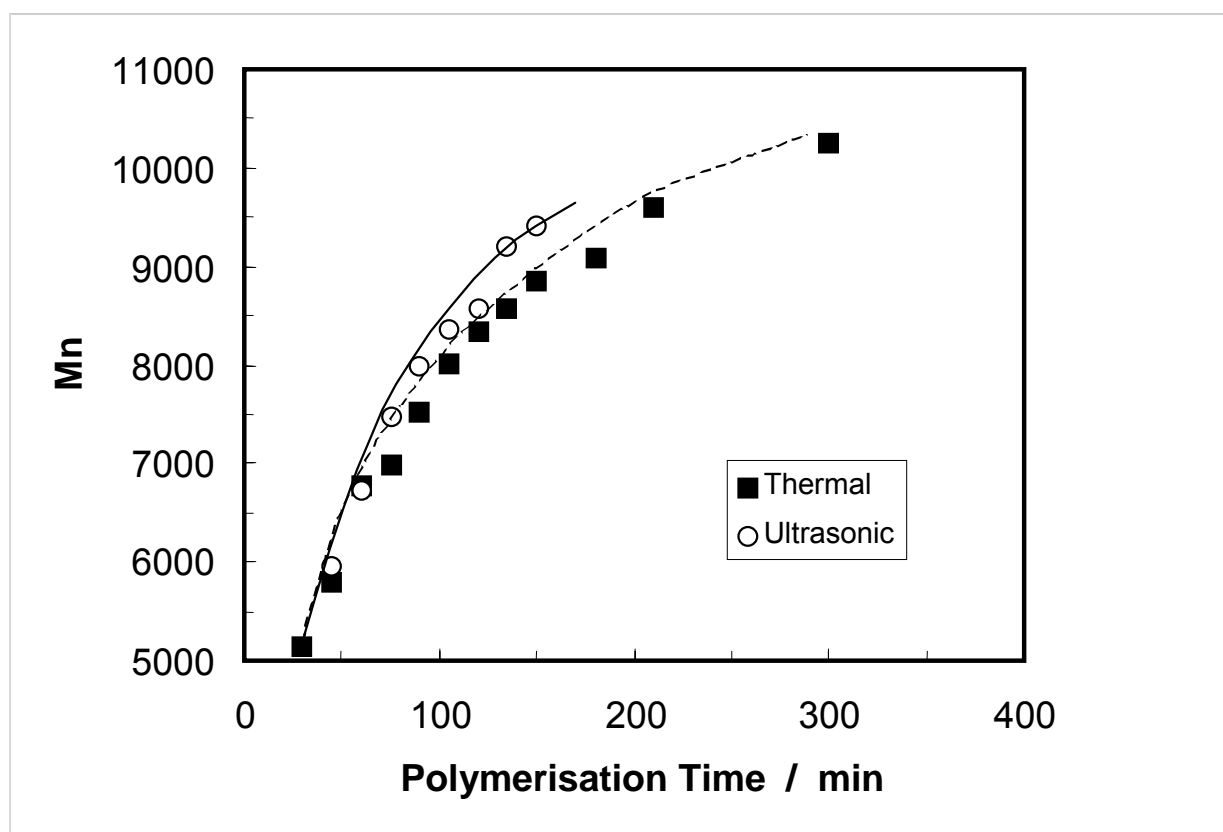


Figure 9

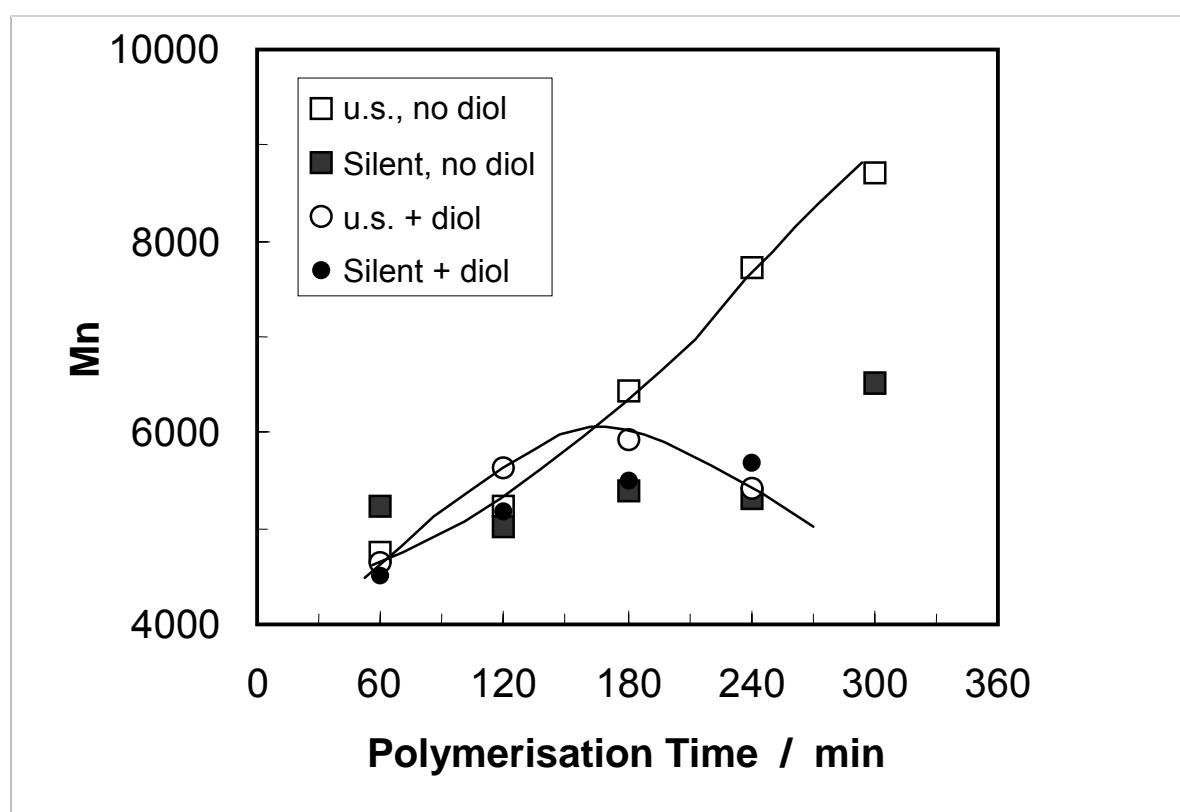


Figure 10

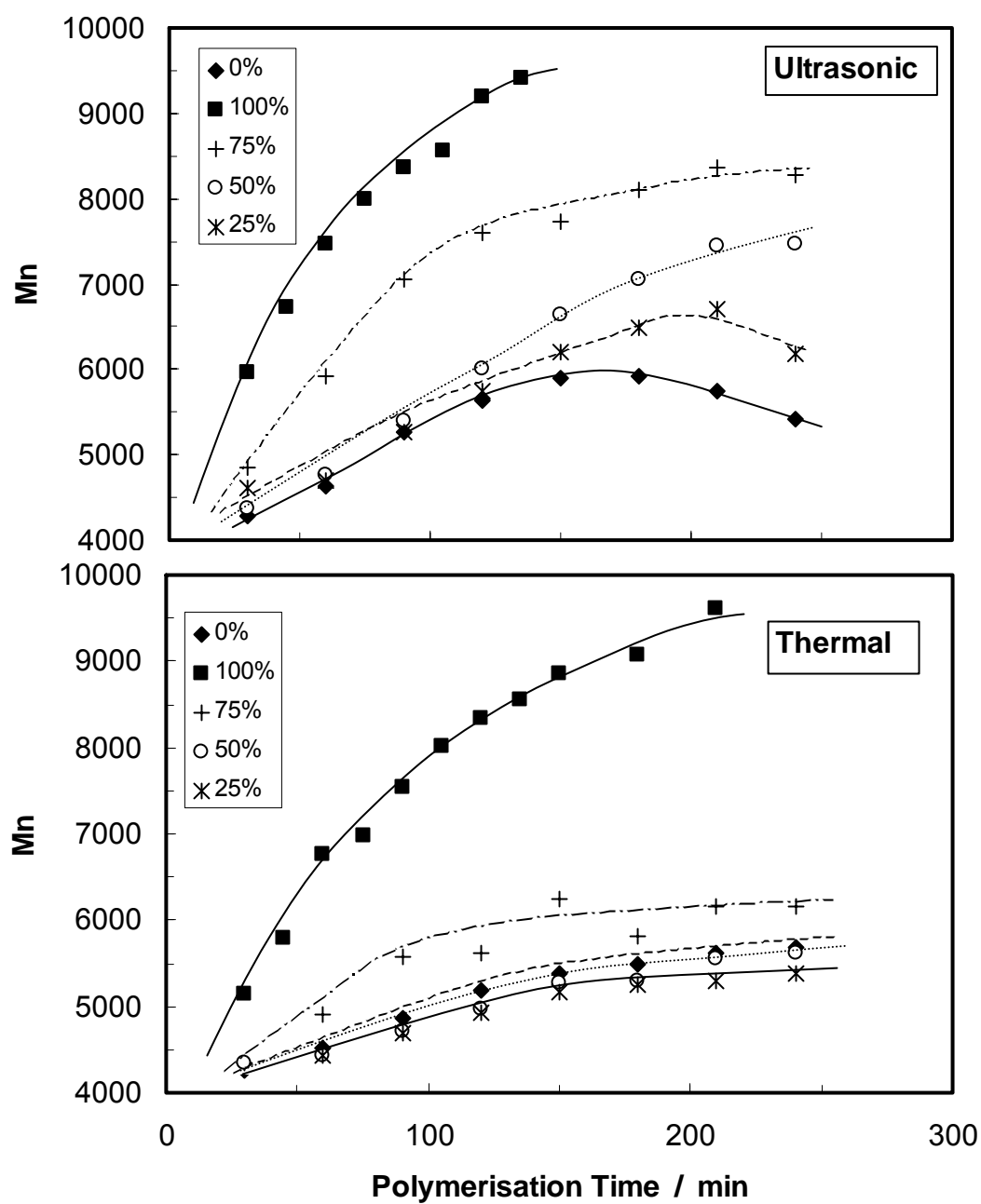


Figure 11

